(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 435 876 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication of patent specification: **08.06.94**

(51) Int. Cl.5: **C11D 11/00**, C11D 3/386, D06B 11/00

(21) Application number: **89909084.9**

(22) Date of filing: **28.07.89**

(86) International application number:
PCT/US89/03274

(87) International publication number:
WO 90/02790 (22.03.90 90/07)

The file contains technical information submitted after the application was filed and not included in this specification

(54) **COMPOSITIONS AND METHODS TO VARY COLOR DENSITY.**

(30) Priority: **15.09.88 US 245123**

(43) Date of publication of application:
10.07.91 Bulletin 91/28

(45) Publication of the grant of the patent:
08.06.94 Bulletin 94/23

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(56) References cited:
EP-A- 0 307 564

(73) Proprietor: **ECOLAB INCORPORATED**
370 North Wabasha Street
Saint Paul, MN 55101(US)

(72) Inventor: **OLSON, Lynne, A.**
Rural Route 1, Box 253
Ellsworth WI 54011(US)
Inventor: **STANLEY, Patricia, M.**
3701 Pillsbury Avenue
Minneapolis, MN 55409(US)

(74) Representative: **Strasse, Maiwald, Meys, Stach & Vonnemann**
Postfach 90 09 54
D-81509 München (DE)

EP 0 435 876 B1

Description

The invention relates to the manufacture of clothing from dyed cellulosic fabrics. More particularly, the invention relates to pumice-free compositions and processes used in the manufacture of a clothing item, preferably from denim fabric dyed with indigo, that can produce in a clothing item a distressed, "used and abused" appearance that is virtually indistinguishable from the appearance of "stone washed" clothing items made by traditional pumice processing.

Clothing made from cellulosic fabrics such as cotton and in particular indigo dyed denim fabrics have been common items of clothing for many years. Such clothing items are typically sold after they are sewn from sized and cut cloth. Such clothes and particularly denim clothing items are stiff in texture due to the presence of sizing compositions used to ease manufacturing, handling and assembling of the clothing items and typically have a fresh dark dyed appearance. After a period of wear, the clothing items, particularly denim, can develop in the clothing panels and on seams, localized areas of variations, in the form of a lightening, in the depth or density of color. In addition a general fading of the clothes can often appear in conjunction with the production of a "fuzzy" surface, some pucker in seams and some wrinkling in the fabric panels. Additionally, after laundering, sizing is substantially removed from the fabric resulting in a softer feel. In recent years such a distressed or "used and abused" look has become very desirable, particularly in denim clothing, to a substantial proportion of the public. To some extent, a limited pre-worn appearance, which has a uniform color density different than the variable color density in the typical stone-washed item, can be produced through prewashing or preshrinking processes.

The preferred methods for producing the distressed "used and abused" look involve stone washing of a clothing item. Stone washing comprises contacting a denim clothing item or items in large tub equipment with pumice stones having a particle size of about 1 to 10 inches (about 2.5-25 cm) and with smaller pumice particles generated by the abrasive nature of the process. Typically the clothing item is tumbled with the pumice while wet for a sufficient period such that the pumice abrades the fabric to produce in the fabric panels, localized abraded areas of lighter color and similar lightened areas in the seams. Additionally the pumice softens the fabric and produces a fuzzy surface similar to that produced by the extended wear of the fabric.

The 1 to 10 inch (about 2.5-25 cm) pumice stones and particulate pumice abrasion by-products can cause significant processing and equipment problems. Particulate pumice must manually be removed from processed clothing items (de-rocking) because they tend to accumulate in pockets, on interior surfaces, in creases and in folds. In the stone washing machine, the stones can cause overload damage to electric motors, mechanical damage to transport mechanisms and washing drums and can significantly increase the requirements for machine maintenance. The pumice stones and particulate material can clog machine drainage passages and can clog drains and sewer lines at the machine site. Further, the abraded pumice can clog municipal sewer lines, can damage sewage processing equipment, and can significantly increase maintenance required in municipal sewage treatment plants. These problems can add significantly to the cost of doing business and to the purchase price of the goods.

In view of the problems of pumice in stone washing, increasing attention has been directed to finding a replacement for stone washing in garment manufacture (see the Wall Street Journal, May 27, 1987, p. 1.). One avenue of investigation involves using a replacement stone such as a synthetic abrasive. In particular, ceramic balls such as those used in ball mills and irregular hard rubber pieces, which can be used without producing abraded by-products, have been experimented with in stone washing processes. These materials reduce the unwanted effects caused by particulate by-product pumice but do not significantly reduce machine damage caused by stones or the required maintenance on stone-containing laundry tubs. As a result, significant attention has been directed to producing a stone-free or pumice-free "stone washed" process that can produce a stone-washed denim look.

One disadvantage in pumice processing is that pumice cannot be used in tunnel washers, the largest commercial washing machines. Pumice cannot be circulated through the tunnel machines due to machine internal geometry. The use of larger-scale tunnel washers could significantly increase the productivity of the processes with the use of a stone or pumice-free composition that produces a genuine "stone-washed" look.

Barbesgarrd et al, U.S. Pat. No. 4,435,307 teach a specific cellulase enzyme that can be obtained from Humicola insolens which can be used in soil removing detergent compositions. Martin et al, European Pat. Application No. 177,165 teach fabric washing compositions containing a surfactant, builders, and bleaches in combination with a cellulase composition and a clay, particularly a smectite clay. Murata et al, U.K. Pat. Application No. 2,095,275 teach enzyme containing detergent compositions comprising an alkali cellulase and typical detergent compositions in a fully formulated laundry preparation. Tai, U.S. Pat. No. 4,479,881

teaches an improved laundry detergent containing a cellulase enzyme in combination with a tertiary amine in a laundry preparation. Murata et al, U.S. Pat. No. 4,443,355 teach laundry compositions containing a cellulase from a cellulosmonas bacteria. Parslow et al, U.S. Pat. No. 4,661,289 teaches fabric washing and softening compositions containing a cationic softening agent and a fungal cellulase in conjunction with other typical laundry ingredients. Suzuki, U.K. Pat. Application No. 2,094,826 teaches detergent laundry compositions containing a cellulase enzyme.

EP 03 07 564 discloses an aqueous process and compositions for obtaining "stone-washed" clothing items. The aqueous treatment can be made from liquid or solid concentrates which contain cellulase enzyme.

Dyed cellulosic clothing (such as denim) have been treated with desizing enzymes, detergents, bleaches, sours and softeners in prewashing and preshrinking processes. These variations are not intended to and do not duplicate the "stone-washed" look. A stone or pumice-free "stone-washed" process that produces the true stone-washed look has yet to be developed.

We have found that the "stone washed" appearance that takes the form of variations in local color density in fabric panels and seams of dyed cellulosic fabrics particularly in denim, clothing items can be substantially obtained using a stone or pumice-free process in which the clothing items are mechanically agitated in a tub with an aqueous composition containing amounts of a cellulase enzyme that can degrade the cellulosic fabric and can release the fabric dye or dyes.

The aqueous treatment compositions are obtained by diluting a novel "stone-wash" liquid or gelled concentrate consisting essentially of a cellulase enzyme and a diluent such as a compatible surfactant composition, a non-aqueous solvent or a thickening agent capable of suspending the cellulase without significant loss of enzymatic activity.

The use of cellulase enzyme preparations is known in laundry cleaning or detergent compositions. Such detergent compositions that are designed for soil removal typically contain surfactants (typically anionic), fillers, brighteners, clays, cellulase and other enzymes (typically proteases, lipases or amylases) and other laundry components to provide a full functioning laundry detergent preparation. The cellulase enzymes in such laundry preparations are typically used (at a concentration less than 500 to 900 CMC units per liter of wash liquor) for the purpose of removing surface fibrils or particles produced by fabric wear which tend to give the fabric a used or faded appearance. The cellulase enzymes in combination with the surfactants used in common laundry compositions for cleaning apparently can remove particulate soil and can restore the new appearance of clothing items. Such compositions are not known to introduce, into clothing, areas of variation in color density which can generally be undesirable in the laundry processing.

For the purpose of this invention, the terms stone-washed appearance and variations in local color depth or density in fabric materials are synonymous. The stone-washed appearance is produced in standard processing in fabric through an abrasion process wherein pumice apparently removes surface bound dye in a relatively small portion of the surface of a garment. Such an abraded area varies from the surrounding color or depth density and is substantially lighter in color. The production of such relatively small local areas of lightness or variation in color depth or density is the goal of both pumice containing stone washing processes in the prior art and Applicant's stone-free chemical treatment methods and compositions.

FIGURE 1 is a graph demonstrating the similarity in visual spectrophotometric character of authentic stone-washed jeans when compared to jeans produced by the compositions and methods of the invention.

The stone free "stone washed" methods of the invention involve contacting clothing items or denim fabric with an aqueous solution containing a cellulase enzyme composition and agitating the treated fabric for a sufficient period of time to produce localized variations in color density in the fabric. The fabric items can be wet by the solution and agitated apart from the bulk aqueous liquors or can be agitated in the liquor. Typically the aqueous solution contains the cellulase enzyme and a cellulase compatible surfactant that increases the wetting properties of the aqueous solution to enhance the cellulase effect.

The aqueous treatment solutions are typically prepared from a liquid or gelled concentrate composition which can be diluted with water at appropriate dilution ratios to formulate the aqueous treatment. The "stone wash concentrate" compositions typically contain the cellulase enzyme and a diluent such as a compatible surfactant, a non-aqueous solvent or a thickening agent that can produce in a treatment liquor a suspension of the cellulose enzyme without significant enzyme activity loss.

Enzymes are a group of proteins which catalyze a variety of typically biochemical reactions. Enzyme preparations have been obtained from natural sources and have been adapted for a variety of chemical applications. Enzymes are typically classified based on the substrate target of the enzymatic action. The enzymes useful in the compositions of this invention involve cellulase enzymes (classified as I.U.B. No. 3.2.1.4., EC numbering 1978). Cellulases are enzymes that degrade cellulose by attacking the C(1→4)

(typically beta) glucosidic linkages between repeating units of glucose moieties in polymeric cellulosic materials. The substrate for cellulase is cellulose, and cellulose derivatives, which is a high molecular weight natural polymer made of polymerized glucose. Cellulose is the major structural polymer of plant organisms. Additionally cellulose is the major structural component of a number of fibers used to produce fabrics including cotton, linen, jute, rayon and ramie, and others.

Cellulases are typically produced from bacterial and fungal sources which use cellulase in the degradation of cellulose to obtain an energy source or to obtain a source of structure during their life cycle. Examples or bacteria and fungi which produce cellulase are as follows: Bacillus hydrolyticus, Cellulobacillus mucosus, cellulobacillus myxogenes, Cellulomonas sp., Cellvibrio fulvus, Celluvibrio vulgaris, Clostridium thermocellulaseum, Clostridium thermocellum, Corynebacterium sp., Cytophaga globulosa, Pseudomonas fluoroescens var. cellulosa, Pseudomonas solanacearum, Bacterioides succinogenes, Ruminococcus albus, Ruminococcus flavefaciens, Sorandium composition, Butyrivibrio, Clostridium sp., Xanthomonas cyamopsidis, Sclerotium bataticola, Bacillus sp., Thermoactinomyces sp., Actinobifida sp., Actinomycetes sp., Streptomyces sp., Arthrobotrys superba, Aspergillus aureus, Aspergillus flavipes, Aspergillus flavus, Aspergillus fumigatus, Aspergillus fuchuenis, Aspergillus nidulans, Aspergillus niger, Aspergillus oryzae, Aspergillus rugulos s, Aspergillus sojae, Aspergillus sydwi, Aspergillus tamaril, Aspergillus terreus, Aspergillus unguis, Aspergillus ustus, Takamine-Cellulase, Aspergillus saitoi, Botrytis cinerea, Botryodipiodia theobromae, Cladosporium cucummerinum, Cladosporium herbarum, Coccospora agricola, Curvularia lunata, Chaetomium thermophile var. coprophile, Chaetomium thermophile var. dissitum, Sporotrichum thermophile, Taromyces amersonii, Thermoascus aurantiacus, Humicola grisea var. thermoidea, Humicola insolens, Malbranchea pulchella var. sulfurea, Myriococcum albomyces, Stilbella thermophile, Torula thermophila, Chaetomium globosum, Dictyosteiium discoideum, Fusarium sp., Fusarium bulbigenum, Fusarium equiseti, Fusarium lateritium, Fusarium lini, Fusarium oxysporum, Fusarium vasinfectum, Fusarium dimerum, Fusarium japonicum, Fusarium scirpi, Fusarium solani, Fusarium moniliforme, Fusarium roseum, Helminthosporium sp., Memnoniella echinata, Humicola fucoatra, Humicola grisea, Monilia sitophila, Monotospora brevis, Mucor pusillus, Mycosphaerella citrulina, Myrothecium verrcaria, Papulaspore sp., Penicillium sp., Penicillium capsulatum, Penicillium chrysogenum, Penicillium, frequentana, Penicillium funicilosum, Penicillium janthinellum, Penicillium luteum, Penicillium piscarium, Penicillium soppi, Penicillium spinulosum, Penicillium turbaturn, Penicillium digitatum, Penicillium expansum, Penicillium pusitlum, Penicillium rubrum, Penicillium wortmanii, Penicillium variabile, Pestalotia palmarum, Pestalotiopsis westerdijkii, Phoma sp., Schizophyllum commune, Scopulariopsis brevicaulis, Rhizopus sp., Sporotricum carnis, Sporotricum pruinosum, Stachybotrys atra, Torula sp., Trichoderma viride (reesei), Trichurus cylindricus, Verticillium albo atrum, Aspergillus cellulosae, Penicillium glaucum, Cunninghamella sp., Mucor mucedo, Rhyzopus chinensis, Coremiella sp., Karlingia rosea, Phytophthora cactorum, Phytophthora citricola, Phytophthora parasitica, Pythium sp., Saprolegniaceae, Ceratocystis ulmi, Chaetomium globosum, Chaetomium indicum, Neurospora crassa, Sclerotium rolfsii, Aspergillus sp., Chrysosporium lignorum, Penicillium notatum, Pyricularia oryzae, Collybia veltipes, Coprinus sclerotigenus, Hydnum henningsii, Irpex lacteus, Polyporus sulphreus, Polyporus betreus, Polystictus hirfutus, Trametes vitata, Irpex consolus, Lentines lepideus, Poria vaporaria, Fomes pinicola, Lenzites styracina, Merulius lacrimans, Polyporus palstris, Polyporus annosus, Polyporus versicolor, Polystictus sanguineus, Poris vailantii, Puccinia graminis, Tricholome fumosum, Tricholome nudum, Trametes sanguinea, Polyporus schweinitzil FR., Conidiophora carebella.

The following cellulase enzyme products are available from the companies indicated: Cellulase AP (Amano Pharmaceutical Co., Ltd.), Cellulosin AP (Ueda Chemical Co., Ltd.), Cellulosin AC (Ueda Chemical Co., Ltd.), Cellulase-Onozuka (Kinki Yakult Seizo Co., Ltd.), Pancellase (Kinki Yakult Seizo Co., Ltd.), Macerozyme (Kinki Yakult Seizo Co., Ltd.), Meicelase (Meiji Selka Kaisha, Ltd.), Celluzyme (Nagase Co., Ltd.), Soluble sclase (Sankyo Co., Ltd.), Sanzyme (Sankyo Co., Ltd.), Cellulase A-12-C (Takeda Chemical Industries, Inc.), Toyo-Cellulase (Toyo Jozo Co., Ltd.), Driserase (Kyowa Hakko Kogyo, Ltd.), Luizyme (Luipold Werk), Takamine-Cellulase (Chemische Fabrik), Wallerstein-Cellulase (Sigma Chemicals), Cellulase Type I (Sigma Chemicals), Cellulase Serva (Serva Laboratory), Cellulase 36 (Rohm and Haas), Miles Cellulase 4,000 (Miles), R & H Cellulase 35, 36, 38 conc (Phillip Morris), Combizym (Nysco Laboratory), Cellulase (Makor Chemicals), Celluclast, Celluzyme, Cellucrust (NOVO Industry), and Cellulase (Gist-Brocades). Cellulase preparations are available from Accurate Chemical & Scientific Corp., Alltech, Inc., Amano International Enzyme, Boehringer Mannheim Corp., Calbiochem Biochems, Carolina Biol. Supply Co., Chem. Dynamics Corp., Enzyme Development, Div. Biddle Sawyer, Fluka Chem. Corp., Miles Laboratories, Inc., Novo Industrials (Biolabs), Plenum Diagnostics, Sigma Chem. Co., Un. States Biochem. Corp., and Weinstein Nutritional Products, Inc.

Cellulase, like many enzyme preparations, is typically produced in an impure state and often is manufactured on a support. The solid cellulase particulate product is provided with information indicating the number of international enzyme units present per each gram of material. The activity of the solid material is used to formulate the treatment compositions of this invention. Typically the commercial preparations contain from about 1,000 to 6,000 CMC enzyme units per gram of product.

A surfactant can be included in the treatment compositions of the invention. The surfactant can increase the wettability of the aqueous solution promoting the activity of the cellulase enzyme in the fabric. The surfactant increases the wettability of the enzyme and fabric. The surfactant facilitates the exclusion of air bubbles from fabric surfaces and the enzyme preparation, and promotes contact between enzyme and fabric surface. The properties of surfactants are derived from the presence of different functional groups.

Surfactants are classified and well known categories including nonionic, anionic, cationic and amphoteric surfactants.

Nonionic surfactants are surfactants having no charge when dissolved or dispersed in aqueous medium. The hydrophilic tendency of nonionic surfactants is derived from oxygen typically in ether bonds which are hydrated by hydrogen bonding to water molecules. Hydrophilic moieties in nonionics can also include hydroxyl groups and ester and amide linkages. Typical nonionic surfactants include alkyl phenol alkoxylates, aliphatic alcohol alkoxylates, carboxylic acid esters, carboxylic acid amides, polyalkylene oxide heteric and block copolymers, and others.

Nonionic surfactants are generally preferred for use in the compositions of this invention since they provide the desired wetting action and do not degrade the enzyme activity. Preferred nonionic surfactants include polymeric molecules derived from repeating units of ethylene oxide, propylene oxide, or mixtures thereof. Such nonionic surfactants include both homopolymeric, heteropolymeric, and block polymeric surfactant molecules. Included within the preferred class of nonionic surfactants are polyethylene oxide polymers, polypropylene oxide polymers, ethylene oxide-propylene oxide block copolymers, ethoxylated C_{1-18} alkyl phenols, ethoxylated C_{1-18} aliphatic alcohols, Pluronic® surfactants, reverse Pluronic® surfactants, and others.

Particularly preferred nonionics include: polyoxyethylene alkyl or alkenyl ethers having alkyl or alkenyl groups of a 10 to 20 average carbon number and having 1 to 20 moles of ethylene oxide added; polyoxyethylene alkyl phenyl ethers having alkyl groups of a 6 to 12 average carbon number and having 1 to 20 moles of ethylene oxide added; polyoxypropylene alkyl or alkenyl ethers having alkyl groups or alkenyl groups of a 10 to 20 average carbon number and having 1 to 20 moles of propylene oxide added; polyoxybutylene alkyl or alkenyl ethers having alkyl groups or alkenyl groups of a 10 to 20 average carbon number and having 1 to 20 moles of butylene oxide added; nonionic surfactants having alkyl groups or alkenyl groups of a 10 to 20 average carbon number and having 1 to 30 moles in total of ethylene oxide and propylene oxide or ethylene oxide and butylene oxide added (the molar ratio of ethylene oxide to propylene oxide or butylene oxide being 0.1/9.9 to 9.9/0.1); or higher fatty acid alkanolamides or alkylene oxide adducts thereof. Less preferred surfactants include anionic, cationic and amphoteric surfactants.

Anionic surfactants are surfactants having a hydrophilic moiety in an anionic or negatively charged state in aqueous solution. Commonly available anionic surfactants include carboxylic acids, sulfonic acids, sulfuric acid esters, phosphate esters, and salts thereof.

Cationic surfactants are hydrophilic moieties wherein the charge is cationic or positive when dissolved in aqueous medium. Cationic surfactants are typically found in amine compounds, oxygen containing amines, amide compositions, and quaternary amine salts. Typical examples of these classes are primary and secondary amines, amine oxides, alkoxylated or propoxylated amines, carboxylic acid amides, alkyl benzyl dimethyl ammonium halide salts and others.

Amphoteric surfactants which contain both acidic and basic hydrophilic structures tend to be of reduced utility in most fabric treating processes.

Solvents that can be used in the liquid concentrate compositions of the invention are liquid produces that can be used for dissolving or dispersing the enzyme and surfactant compositions of the invention. Because of the character of the preferred nonionic surfactants, the preferred solvents are oxygen containing solvents such as alcohols, esters, glycol, glycol ethers, etc. Alcohols that can be used in the composition of the invention include methanol, ethanol, isopropanol, tertiary butanol, etc. Esters that can be used include amyl acetate, butyl acetate, ethyl acetate, esters of glycols, and others. Glycols and glycol ethers that are useful as solvents in the invention include ethylene glycol, propylene glycol, and oligomers and higher polymers of ethylene or propylene glycol in the form of polyethylene or polypropylene glycols. In liquid concentrates the low molecular weight oligomers are preferred.

The cellulases are deactivated in some cases in the presence of heavy metal ions including copper, zinc, chromium, mercury, lead, manganese, or silver ions or their compounds. Various metal chelating

agents and metal-precipitating agents are effective against these inhibitors. They include, for example, divalent metal ion sequestering agents as listed below with reference to optional additives as well as magnesium silicate and magnesium sulfate.

Cellobiose, glucose and gluconolactone can act as an inhibitor. It is preferred to avoid the co-presence of those saccharides with the cellulase if possible. In case the co-presence is unavoidable, it is necessary to avoid the direct contact of the saccharides with the cellulase by, for example, coating them.

Long chain fatty acid salts and cationic surfactants act as the inhibitors in some cases. However, the co-presence of these substances with the cellulase is allowable if the direct contact of them is prevented by some means such as tableting or coating.

The above-mentioned masking agents and methods may be employed, if necessary, in the present invention.

The activators vary depending on variety of the cellulases. In the presence of proteins, cobalt and its salts, magnesium and its salts, and calcium and its salts, potassium and its salts, sodium and its salts or monosaccharides such as mannose and xylose, the cellulases are activated and their deterging powers can be improved.

The antioxidants include, for example, tert-butylhydroxytoluene, 4,4'-butylidenebis(6-tert-butyl-3-methylphenol), 2,2'-butylidenebis(6-tert-butyl-4-methylphenol), monostyrenated cresol, distyrenated cresol, monostyrenated phenol, distyrenated phenol and 1,1-bis(4-hydroxyphenyl)cyclohexane.

The solubilizers include, for example, lower alcohols such as ethanol, benzenesulfonate salts, lower alkylbenzenesulfonate salts such as p-toluenesulfonate salts, glycols such as propylene glycol, acetylbenzenesulfonate salts, acetamides, pyridinedicarboxylic acid amides, benzoate salts and urea.

The detergent composition of the present invention can be used in a broad pH range of about 6.5 to 10, preferably 6.5 to 8.

The composition may contain 0-50 wt-% of one or more builder components selected from the group consisting of alkali metal salts and alkanolamine salts of the following compounds: phosphates such as orthophosphate, pyrophosphate, tripolyphosphate, metaphosphate, hexametaphosphate and phytic acid; phosphonates such as ethane-1,1-diphosphonate, ethane-1,1,2-triphosphonate, ethane-1-hydroxy-1,1-diphosphonate and its derivatives, ethanehydroxy-1,1,2-triphosphonate, ethane-1,2-dicarboxy-1,2-diphosphonate and methanehydroxyphosphonate; phosphonocarboxylates such as 2-phosphonobutane-1,2-dicarboxylate, 1-phosphonobutane-2,3,4-tricarboxylate and α-methylphosphonosuccinate; salts of amino acids such as aspartic acid, glutamic acid and glycine; aminopolyacetates such as nitrilotriacetate, ethylenediaminetetraacetate, diethylenetriaminepentaacetate, iminodiacetate, glycol ether diamine tetraacetate, hydroxyethyliminodiacetate; high molecular electrolytes such as polyacrylic acid, polyaconitic acid, polyitaconic acid, polycitraconic acid, polyfumaric acid, polymaleic acid, polymesaconic acid, poly-α-hydroxyacrylic acid, polyvinylphosphonic acid, sulfonated polymaleic acid, maleic anhydride/diisobutylene copolymer, maleic anhydride/styrene copolymer, maleic anhydride/methyl vinyl ether copolymer, maleic anhydride/ethylene copolymer, maleic anhydride/ethylene crosslinked copolymer, maleic anhydride/vinyl acetate copolymer, maleic anhydride/acrylonitrile copolymer, maleic anhydride/acrylic ester copolymer, maleic anhydride/butadiene copolymer, maleic anhydride/isoprene copolymer, poly-β-ketocarboxylic acid derived from maleic anhydride and carbon monoxide, itaconic acid/ethylene copolymer, itaconic acid/aconitic acid copolymer, itaconic acid/maleic acid copolymer, itaconic acid/acrylic acid copolymer, malonic acid/methylene copolymer, mesaconic acid/fumaric acid copolymer, ethylene glycol/ethylene terephthalate copolymer, vinylpyrrolidone/vinyl acetate copolymer, 1-butene-2,3,4-tricarboxylic acid/itaconic acid/acrylic acid copolymer, polyester polyaldehydocarboxylic acid containing quaternary ammonium group, cis-isomer of epoxysuccinic acid, poly[N,N-bis(carboxymethyl)acrylamide], poly(hydroxycarboxylic acid), starch/succinic acid or maleic acid or terephthalic acid ester, starch/phosphoric acid ester, dicarboxystarch, dicarboxymethylstarch, and cellulose/succinic acid ester; non-dissociating polymers such as polyethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone and cold water soluble, urethanated polyvinyl alcohol; and salts of dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and decane-1,10-dicarboxylic acid; salts of diglycolic acid, thiodiglycolic acid, oxalacetic acid, hydroxydisuccinic acid, carboxymethylhydroxysuccinic acid and carboxymethyltartronic acid; salts of hydroxycarboxylic acids such as glycolic acid, malic acid, hydroxypivalic acid, tartaric acid, citric acid, lactic acid, gluconic acid, mucic acid, glucuronic acid and dialdehydrostarch oxide; salts of itaconic acid, methylsuccinic acid, 3-methylglutaric acid, 2,2-dimethymalonic acid, maleic acid, fumaric acid, glutamic acid, 1,2,3-propanetricarboxylic acid, aconitic acid, 3-butene-1,2,3-tricarboxylic acid, butane-1,2,3,4-tetracarboxylic acid, ethanetetracarboxylic acid, ethenetetracarboxylic acid, n-alkenylaconitic acid, 1,2,3,4-cyclopentanetetracarboxylic acid, phthalic acid, trimesic acid, hemimellitic acid, pyromellitic acid, benzenehexacarboxylic acid, tetrahydrofuran-1,2,3,4-tetracarboxylic acid and tetrahydrofuran-2,2,5,5-

tetracarboxylic acid; salts of sulfonated carboxylic acids such as sulfoitaconic acid, sulfotricarballylic acid, cysteic acid, sulfoacetic acid and sulfosuccinic acid; carboxymethylated sucrose, lactose and raffinose, carboxymethylated pentaerythritol, carboxymethylated gluconic acid, condensates of polyhydric alcohols or sugars with maleic anhydride or succinic anhydride, condensates of hydroxycarboxylic acids with maleic anhydride or succinic anhydride, and the like.

The cellulase treatment compositions of the invention can be manufactured in the form of a thickened liquid or a gel. Common organic and inorganic compositions can be used to produce the thickened or gelled product form. Such a product form is useful in enzyme preparations wherein the enzyme tends to be salted out by the concentration of inorganic or organic buffer components. The thickened or gelled compositions tend to maintain the uniformity of the enzyme containing compositions and can ensure that the enzyme treatments are uniform. A non-uniform product can result in either large excesses of enzyme or absence of enzyme. Such thickeners include organic and naturally occurring polymers such as ethylene vinyl acetate copolymers, polyethylene waxes, acrylic polymers, cellulosic polymers including carboxymethyl cellulose, carboxyethyl cellulose, cellulose acetates, ethoxylated cellulose, alkanolamides, waxy alcohols, and others; magnesium aluminum silicates, bentonite clays, fumed silica, xanthan guar gum, algin derivatives, polyvinyl pyrrolidone, di- and tristearate salts, and other conventional thickeners.

We have found that the preferred mode of contacting the dyed cellulosic fabrics with the treatment compositions of the invention is to maintain as set forth above the concentration of the enzyme in the aqueous treating solution at least 1,500 CMC units of enzyme per liter of solution. Additionally we have found that controlling the ratio between treating solution and fabric is important in optimizing the treatment. We have found that maintaining the amount of aqueous treatment to about 1 to about 10 milliliters of treatment solution per gram of fabric, preferably about 2 to 8 milliliters of aqueous solution per gram of dyed cellulosic fabric, aids in the economic treatment of the dyed cellulosic fabrics, primarily indigo dyed denim, to obtain the optimal used and abused appearance.

In somewhat greater detail, the clothing items can be contacted with an aqueous solution containing cellulase enzyme and a surfactant to promote the action of the cellulase for a sufficient time to produce local variations in color density in the surface of the fabric. The amount of solution used to treat the clothing items typically depends on the ratio of cellulase in the product and the dry weight of the clothing items to be washed. Typically the solutions used in the methods of the invention can contain a minimum of about 1,500 CMC units of cellulase per liter, preferably 1,750 to 7,500 units per liter, most preferably 2,000 to 6,000 units per liter to obtain the "stone-washed" look. In a preferred mode the newly sewn jeans can be desized at 150° F. (65.6° C.) for 10 minutes, rinsed, contacted with about 1,500 to 6,000 CMC u/l of enzyme for 45 minutes at 160° F. (71.1° C.) while tumbling the jeans, washed, rinsed, softened and dried. A preferred method is as follows:

Step	Time	Temperature	Machine Water Level	Product
Shakeout Desize, stand.	1 min.	65.6° C.	76.2 cm	Desizer
Rotation	10 min.	65.6° C.	76.2 cm	Desizer
Drain Rinse	3 min.	65.6° C.	76.2cm	
Drain Abrade	45min.	71.1° C.	15.2 cm	Enzyme at 2000 CMC U/L
Drain Rinse	2 min.	65.6° C.	63.5 cm	-------
Drain Wash	5 min.	54.4° C.	30.5 cm	Bleach
Drain Rinse	3 min.	43.3° C.	55.9 cm	-------
Drain Rinse	3 min.	43.3° C.	55.9 cm	-------
Drain Sour/Soft	5 min.	37.8° C.	30.5 cm	
Drain Extract	4 min.			
TOTAL TIME	70 min. (30 second drains)			

The treatment solutions used to contact the clothes can typically have the following ingredients.

Table 1

Aqueous Treating Compositions			
Ingredient	Useful	Preferred	Most Preferred
Cellulase Enzyme*	At least 1,500	2,500-30,000	6,000-20,000
Cellulase Enzyme**	--	0.5-3 (0.2-1.4 kg)	0.75-2.5 (0.3-1.2 kg)
Surfactant	0-1,000 ppm	10-900 ppm	15-750 ppm
Aqueous*** treatment	1-10	2-8 ml/gram	2-4 ml/gram

* Amounts in CMC units per liter.
** Lb. (kg) of enzyme/100 lbs. (45.4 kg) of fabric.
*** Amounts in ml of aqueous treatment per gram of fabric.

Table 2

Concentrate Compositions			
Ingredient	Useful	Preferred	Most Preferred
Cellulase Enzyme	1-90 wt-%	2-80 wt-%	5-75 wt-%
Surfactant	99-0 wt-%	98-5 wt-%	95-10 wt-%
Solvent	Balance	Balance	Balance

Table 5

Gelled Treatment Concentrate	
Ingredient	Wt-%
Liquid Enzyme	48
Monosodium phosphate	25.57
Disodium phosphate	14.43
Xanthan gum	0.48
Water	11.52

Table 6

Liquid Concentrate	
Ingredient	Wt-%
Liquid enzyme	70.0
Sodium acetate	28.59
Acetic acid	1.41

Table 7

Liquid Enzyme Product Analysis	
Ingredient	Wt-%
Solids	27.9
Propylene glycol	24.0
Sorbitol	4.3
Alkali metal	0.3
Water	48.1
pH of 1% aqueous solution	6.6
Enzyme activity	1,000 CMC U/g

Table 8

Liquid Enzyme Product Analysis	
Ingredient	Wt-%
Solids	49.2
Sorbitol	21.5
Alkali metal	1.9
Phosphorous	0.2
Water	50.8
pH of 1% aqueous solution	5.7
Enzyme activity	1,600 CMC U/g

Tables 5-8 disclose useful gelled and liquid enzyme compositions that can be used in obtaining the "stone washed" look. The liquid enzyme products used in Tables 5 and 6 are set forth in Table 7.

The liquid concentrate compositions of this invention can be formulated in commonly available industrial mixers. Typically a solution of the surfactant is prepared in the solvent and into the surfactant solution is added the cellulase enzyme sufficiently slowly to create a uniform enzyme dispersion in the solvent. The concentrates can be packaged in typical inert packaging such as glass, polyethylene or polypropylene, or PET. Care should be taken such that agitation does not significantly reduce the activity of the cellulase enzyme.

All of the liquid and gelled concentrate compositions of the invention can include additional ingredients that preserve or enhance the enzyme activity in the pumice-free stone wash processes of the invention.

The compositions of this invention are typically diluted in water in household, institutional, or industrial machines having a circular drum held in a horizontal or vertical mode in order to produce the "stone-washed" appearance without the use of pumice or other particulate abrasive. Most commonly the denim or other fabric clothing items are added to the machine according to the machine capacity per the manufacturer's instructions. Typically the clothes are added prior to introducing water into the drum but the clothes can be added to water in the machine or to the pre-diluted treatment composition. The clothing is contacted with the treatment composition and agitated in the machine for a sufficient period to ensure that the clothing has been fully wetted by the treatment composition and to ensure that the cellulase enzyme has had an opportunity to cleave cellulose in the fabric material. At this time if the treatment composition is to be reused, it is often drained from the tub and saved for recycle. If the treatment composition is not to be reused, it can remain on the clothing for as long as needed to produce color variation. Such treatment periods are greater than 5 minutes, greater than 30 minutes and up to 720 minutes, depending on amount of enzyme, during all or part of the mechanical machine action used to produce in the cellulase treated fabric the variations in color density. We believe that there is an interaction between the cellulase modified fabric and mechanical tumbling or action which removes cellulose from the fabric surface and the indigo dye to create a variation in color density from place to place on fabric panels and seams. Further, the action of the enzyme appears to cause puckering in the seams and a creation of a soft, wrinkled look in fabric panels.

The above specification provides a discussion of the compositions of the invention and methods of making and using the compositions in the "stone-washing" of fabric clothing items. The following Examples provide specific details with respect to the compositions and methods of the invention and include a best mode.

Examples I-III

Into a Milnor 35 lb. (15.9 kg) capacity washing machine was placed new blue denim Jeans and into the machine was placed 25 gallons (94.7 liters) of 120° F. (48.9° C.) water containing an amylase enzyme desizing stripper composition. The contents of the machine was agitated for 9 minutes and the aqueous solution was dumped. Into the machine was placed 17 gallons (64.4 liters) of water at 120° F. (48.9° C.) containing an amount of cellulase enzyme (see Table 5 below) and 10 milliliters of an aqueous solution containing 23 wt-% H_2SiF_6 and 50 wt-% citric acid. The jeans were agitated in the celluzyme composition for 1 hour and the aqueous composition was dumped. The jeans were then rinsed in three successive water rinses at 120° F. (48.9° C.), 110° F. (43.3° C.), and a final rinse at 100° F. (37.8° C.) containing 80 milliliters of softening agent and 5 milliliters of the sour product.

Table 9

Example	Concentrate Grams	CMCU/L[1] 6,000	CMCU/LB[2]	CMCU/ Pair[3]	Grams/ Pair[4]
I	200	7,459	32,000	48,000	20
II	300	11,189	48,000	72,000	30
III	400	14,918	64,000	96,000	40

---

[1] Carboxymethyl cellulose units/liter of solution

[2] Carboxymethyl cellulose units/pound (0.45 kg) of fabric

[3] Carboxymethyl cellulose units/pair of jeans

[4] Grams of concentrate/pair of jeans

Table 10

Visible Spectrophotometer Scan of Stone Washed Jeans and Product of Example II

Wave Length	Stone Washed Jeans	Example II	Differences
380	11.50	11.01	-0.49
390	15.71	15.32	-0.39
400	18.57	18.49	-0.08
410	21.70	21.99	0.69
420	23.01	24.22	1.20
430	22.96	24.24	1.28
440	22.19	23.53	1.34
450	21.31	22.62	1.31
460	20.38	21.64	1.26
470	19.43	20.63	1.20
480	18.60	19.71	1.10
490	17.91	18.92	1.01
500	17.18	18.08	0.90
510	16.35	17.13	0.77
520	15.40	16.06	0.66

530	14.40	14.92	0.52
540	13.47	13.88	0.41
550	12.77	13.08	0.31
560	12.32	12.60	0.28
570	11.94	12.15	0.21
580	11.42	11.59	0.17
590	10.85	10.97	0.12
600	10.35	10.39	0.04
610	9.95	9.94	-0.01
620	9.60	9.56	-0.04
630	9.15	9.07	-0.08
640	8.75	8.64	-0.11
650	8.44	8.30	-0.14
660	8.35	8.21	-0.14
670	8.66	8.58	-0.08
680	9.70	9.73	0.03
690	11.83	12.12	0.29
700	15.83	16.60	0.77
710	22.62	23.99	1.37
720	32.13	33.84	1.71
730	42.55	43.96	1.41
740	51.26	51.92	0.65
750	57.04	57.03	-0.01

Detailed Discussion of the Drawings

Fig. 1 is a graphical representation of the data in the above table. The graph appears to be a single line consisting of dots and dashes, however the graph shows that the percent reflectance of the stone washed denims and the denims produced using the compositions and methods of this invention are virtually identical. The differences shown in column 4 of the above table indicate that at certain wavelengths minor differences occur, however the curves are virtually superimposable.

The above disclosure, Examples and data provide a complete discussion of the invention, which resides in the claims hereinafter appended.

Claims

1. A liquid concentrate composition that can be used in aqueous solution to introduce, into the surface of dyed cellulosic fabrics, local areas of variations in color density, which consists essentially of:
   a) 25-90 wt-% of a cellulase enzyme composition;
   b) 0.01-10 wt-% of a thickening agent; and
   c) 0.1-50 wt-% of a buffer that can maintain the pH of the aqueous solution to about the optimum pH for enzyme activity;
   wherein the variation in color density is substantially the same as that produced by conventional pumice stone processing.

2. The composition of claim 1 wherein the cellulase is a fungal cellulase.

3. The composition of claim 1 which additionally contains an anti-redeposition agent.

4. The composition of claim 1 wherein the composition additionally contains an anti-foaming agent

5. The composition of claim 1 wherein the thickening agent is a xanthan gum.

6. A liquid concentrate composition that can be used in aqueous solution to introduce, into the surface of dyed cellulosic fabric, local areas of variation and color density which consists essentially of:
a) an amount of cellulase enzyme composition to provide to an aqueous treatment solution at least 1,500 CMC units of enzyme per liter of solution;
b) an oxygen containing diluent, preferably an alcoholic diluent and
c) a buffer that can maintain the pH of the aqueous solution at about the cellulase enzyme optimum pH;
wherein the variation in color density is substantially the same as that produced by conventional pumice stone processing.

7. The composition of claim 6 wherein the alcoholic diluent comprises a C_{1-4} alkanol.

8. The composition of claim 7 wherein the C_{1-4} alkanol comprises a diol.

9. The composition of claim 8 wherein the diol comprises propylene glycol.

10. A method of introducing into the surface of dyed cellulosic fabrics, localized area of variation and color density, which method comprises contacting the fabric with an aqueous composition made from a concentrate, said aqueous composition consisting essentially of:
a) a major proportion of water;
b) at least 25 wt-% of a cellulase enzyme composition in said concentrate and at least 1,500 CMC units of cellulase enzyme per liter of aqueous composition; and
c) a buffer that can maintain the pH of the aqueous solution at about the cellulase enzyme optimum pH;
wherein the fabric is contacted with the aqueous composition at a ratio of about 1-10, preferably 2-8 milliliters of aqueous solution per gram of dyed cellulosic fabric, and wherein the variation in color density is substantially the same as that produced by conventional pumice stone processing.

11. The method of claim 10 wherein the fabric is contacted with the aqueous solution for at least 5 minutes.

12. The method of claim 10 wherein the cellulase is a fungal cellulase.

13. The method of claim 10 wherein the fabric is indigo dyed denim.

Patentansprüche

1. Flüssige Konzentratzusammensetzung, die in wässriger Lösung zur Einführung lokaler Bereiche geänderter Farbdichte in die Oberfläche von gefärbten Cellulosegeweben, verwendet werden kann und im wesentlichen besteht aus:
a) 25-90 Gew.-% einer Cellulase-Enzymzusammensetzung;
b) 0,01-10 Gew.-% eines Verdickungsmittels; und
c) 0,1-50 Gew.-% eines Puffers, der den pH der wässrigen Lösung ungefähr auf dem für die Enzymaktivität optimalen pH hält;
wobei die Änderung in der Farbdichte im wesentlichen dieselbe ist, wie durch herkömmliche Bimssteinbehandlung hervorgerufen.

2. Zusammensetzung nach Anspruch 1, worin die Zellulase eine Pilzcellulase ist.

3. Zusammensetzung nach Anspruch 1, die zusätzlich ein Mittel gegen Wiederablagerung enthält.

4. Zusammensetzung nach Anspruch 1, worin die Zusammensetzung zusätzlich ein Entschäumungsmittel enthält.

5. Zusammensetzung nach Anspruch 1, worin das Verdickungsmittel ein Xanthangummi ist.

6. Flüssige Konzentratzusammensetzung, die in wässriger Lösung zur Einführung lokaler Bereiche geänderter Farbdichte in die Oberfläche von gefärbten Cellulosegeweben, verwendet werden kann und im wesentlichen besteht aus:
   a) einer Menge an Cellulase-Enzym-Zusammensetzung, die mindestens 1500 CMC Enzymeinheiten je Liter der Lösung zur Verfügung stellt;
   b) einem Sauerstoff enthaltenden Verdünnungsmittel, vorzugsweise einem alkoholischen Verdünnungsmittel und
   c) einem Puffer, der den pH der wässrigen Lösung ungefähr auf dem für das Cellulase-Enzym optimalen pH hält;
   wobei die Änderung der Farbdichte im wesentlichen dieselbe ist wie durch herkömmliche Bimssteinbehandlung hervorgerufen.

7. Zusammensetzung nach Anspruch 6, wobei das alkoholische Verdünnungsmittel ein C_{1-4}-Alkanol umfaßt.

8. Zusammensetzung nach Anspruch 7, wobei das C_{1-4}-Alkanol ein Diol umfaßt.

9. Zusammensetzung nach Anspruch 8, wobei das Diol Propylenglycol umfaßt.

10. Verfahren zur Einbringung eines lokalen Bereichs geänderter Farbdichte in die Oberfläche von gefärbten Cellulosegeweben, wobei das Verfahren ein Inkontaktbringen des Gewebes mit einer aus einem Konzentrat hergestellten wässrigen Zusammensetzung umfaßt, worin die wässrige Zusammensetzung im wesentlichen besteht aus:
   a) einem Hauptanteil Wasser;
   b) mindestens 25 Gew.-% Cellulase-Enzym-Zusammensetzung in dem Konzentrat und zumindest 1500 CMC Einheiten Cellulase-Enzym je Liter der wässrigen Zusammensetzung; und
   c) einen Puffer, der den pH der wässrigen Lösung ungefähr auf dem für das Cellulase-Enzym optimalen pH hält;
   wobei das Gewebe mit der wässrigen Zusammensetzung in einem Verhältnis von ungefähr 1-10, vorzugsweise 2-8 ml wässriger Lösung je Gramm gefärbtem Cellulosegewebe kontaktiert wird, und wobei die Änderung der Farbdichte im wesentlichen dieselbe ist wie durch herkömmliche Bimssteinbehandlung hervorgerufen.

11. Verfahren nach Anspruch 10, wobei das Gewebe für zumindest 5 Minuten mit der wässrigen Lösung in Kontakt kommt.

12. Verfahren nach Anspruch 10, wobei die Cellulase eine Pilzcellulase ist

13. Verfahren nach Anspruch 10, wobei das Gewebe indigogefärbter Jeansstoff ist.

Revendications

1. Composition liquide concentrée pouvant être utilisée dans une solution aqueuse pour créer, à la surface de tissus cellulosiques teints, des zones localisées de variations de densité de couleur, constituée essentiellement de :
   a) 25 à 90 % en poids d'une composition d'enzyme cellulase ;
   b) 0,01 à 10 % en poids d'un agent épaississant ; et
   c) 0,1 à 50 % en poids d'un tampon capable de maintenir le pH de la solution aqueuse environ au niveau du pH optimal pour l'activité enzymatique ;
   dans laquelle la variation de la densité de couleur est sensiblement la même que celle produite par le traitement classique à la pierre ponce.

2. Composition selon la revendication 1, dans laquelle la cellulase est une cellulase fongique.

3. Composition selon la revendication 1, contenant en outre un agent anti-redéposition.

4. Composition selon la revendication 1, dans laquelle la composition contient en outre un agent anti-mousse.

5. Composition selon la revendication 1, dans laquelle l'agent épaississant est une gomme de xanthane.

6. Composition liquide concentrée pouvant être utilisée dans une solution aqueuse pour créer à la surface de tissus cellulosiques, des zones localisées de variations de densité de couleur, essentiellement constituée de :
   a) une quantité d'une composition d'enzyme cellulase pour fournir à une solution de traitement aqueux au moins 1 500 unités CMC d'enzyme par litre de solution ;
   b) un diluant contenant de l'oxygène, de préférence un diluant alcoolique ; et
   c) un tampon capable de maintenir le pH de la solution aqueuse au niveau du pH optimal pour l'enzyme de cellulase ; dans lequel la variation de la densité de couleur est sensiblement la même que celle produite par le traitement classique à la pierre ponce.

7. Composition selon la revendication 6, dans laquelle le diluant alcooilque comprend un alcanol en C_{1-4}.

8. Composition selon la revendication 8, dans laquelle l'alcanol en C_{1-4} comprend un diol.

9. Composition selon la revendication 8, dans laquelle le diol comprend du propylène glycol.

10. Procédé pour créer dans la surface de tissus cellulosiques teints, des zones localisées de variation de la densité de couleur, ledit procédé comprenant les étapes consistant à mettre la tissu en contact avec une composition aqueuse formée à partir d'un concentré, ladite composition étant essentiellement constituée de :
    a) une majeure partie d'eau ;
    b) au moins 25 % en poids d'une composition d'enzyme cellulase dans ledit concentré et au moins 1 500 unités CMC d'enzyme cellulase par litre de composition aqueuse ; et
    c) un tampon capable de maintenir le pH de la solution aqueuse au niveau du pH optimal pour l'enzyme de cellulase ; dans laquelle le tissu est mis en contact avec la composition aqueuse selon un rapport compris environ entre 1 et 10, de préférence entre 2 et 8 millilitres de solution aqueuse par gramme de tissu cellulosique teint, et dans laquelle la variation de densité de couleur est sensiblement la même que celle produite par le traitement classique à la pierre ponce.

11. Procédé selon la revendication 10, dans lequel le tissu est mis en contact avec la solution aqueuse pendant au moins 5 minutes.

12. Procédé selon la revendication 10, dans lequel la cellulase est une cellulase fongique.

13. Procédé selon la revendication 10, dans lequel le tissu est du denim teint en bleu indigo.

VISUAL
SPECTRO PHOTO METRIC
COMPARISON OF STONE-WASHED
JEANS AND JEANS OF THE INVENTION

• • • • • • • • PRODUCT OF EXAM. II

— — — — — — STANDARD STONE-WASHED JEANS